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<p>(21) International Application Number: PCT/GB94/01184 (22) International Filing Date: 1 June 1994 (01.06.94) (30) Priority Data: 9311399.1 2 June 1993 (02.06.93) GB (71) Applicant (for all designated States except US): ZENECA LIMITED [GB/GB]; 15 Stanhope Gate, London W1Y 6LN (GB). (72) Inventors; and (73) Inventors/Applicants (for US only): HAMMOND, Timothy [GB/GB]; 12 Cragside, Sedgefield, Stockton on Tees, Cleveland TS21 2DQ (GB). LIGGAT, John, Jamieson [GB/GB]; 64 Briggs Avenue, Middlesbrough, Cleveland TS6 6XN (GB). MONTADOR, James, Henry [GB/GB]; 14 Northpark, Owington Farm, Billingham, Cleveland TS23 3SU (GB). WEBB, Andrew [GB/GB]; 16 Spell Close, Yarm TS15 9SD (GB). (74) Agent: LOCKE, Timothy, John; Intellectual Property Group, Zeneca Bioproducts, P.O. Box 2, Belasis Avenue, Billingham TS23 1YN (GB).</p>	<p>(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, GE, HU, JP, KG, KP, KR, KZ, LK, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  Published With international search report.</p>	
<p>(54) Title: POLYESTER COMPOSITION (57) Abstract  Polyester composition comprising a biodegradable polyester and a plasticising quantity of at least one plasticiser selected from the group: high-boiling esters of polybasic acids; phosphoric acid derivatives; phosphorous acid derivatives; phosphonic acid derivatives; substituted fatty acids; high-boiling glycols, polyglycols, polyoxyalkylenes and glycerol each optionally substituted and optionally terminally esterified; pentaerythritols and derivatives; sulphonic acid derivatives; epoxy derivatives; chlorinated paraffins; polymeric esters; Walflex-But®; provided that citrates does not include doubly esterified hydroxycarboxylic acids having at least 3 ester groups in its molecule and further provided that glycerols do not include glycerol triacetate and glycerol diacetate.</p>		

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**POLYESTER COMPOSITION**

THIS INVENTION relates to a polyester composition and in particular to such a composition containing biodegradable polyester and plasticiser.

5 Biodegradable polyesters for example the microbiologically produced polyhydroxyalkanoates can be adapted by the use of plasticiser compounds for applications where improved impact strength, improved elongation to break and improved ductility are important. Since such compounds should preferably also be biodegradable, many of the  
10 plasticisers used in synthetic polymer processing are not suitable for biodegradable polymers. Most commonly the glyceryl ester triacetin (glycerol triacetate) is used, but it is more volatile than is ideal during melt processing or storage at high ambient temperatures. Recently, a new plasticiser called Estaflex<sup>®</sup> (acetyl tri-n-butyl citrate) has been  
15 introduced for polyhydroxyalkanoates which is an improvement over triacetin, however, alternatives to these compounds are continually sought for further improvements in physical properties of the polymer, improvements in the biodegradability and resistance to migration in the polymer, improvements in flexibility, mobility and permanence, and  
20 economic benefits. In looking for new plasticisers the applicants have unexpectedly found that a number of plasticisers or materials used in conventional plasticised systems are useful plasticisers of biodegradable polyesters.

Thus, according to the present invention there is provided a  
25 polyester composition comprising a biodegradable polyester and a plasticising quantity of at least one plasticiser selected from the group : high-boiling esters of polybasic acids; phosphoric acid derivatives; phosphorous acid derivatives; phosphonic acid derivatives; substituted fatty acids; high-boiling glycols, polyglycols, polyoxyalkylenes and  
30 glycerol each optionally substituted and optionally terminally esterified; pentaerythritols and derivatives; sulphonic acid derivatives; epoxy derivatives; chlorinated paraffins; polymeric esters; Wolflex-But<sup>®</sup>; provided that citrates does not include doubly esterified hydroxycarboxylic acids having at least 3 ester groups in its molecule and

further provided that glycerols does not include glycerol triacetate and glycerol diacetate.

In the description, examples and claims herein a \* indicates a tradename or registered trademark.

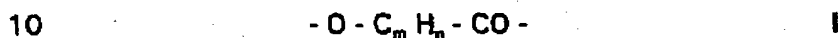
5           The majority of plasticisers used in this invention are known in the art as plasticisers of other materials. A plasticiser is a material which when added to a polymer composition makes an improvement in the ductility of the polymer. It is generally the case with most plasticised polymer systems that the extent of the plasticising effect is in direct  
10           correlation with the glass transition temperature ( $T_g$ ) of the plasticised material, i.e. the lower the  $T_g$  the greater the plasticising effect. It has now been found that in the biodegradable polyesters of the present invention, the glass transition temperature is not a predictor of the extent of beneficial effect of the plasticiser of the polymer, and surprisingly the plasticisers of the present invention are unexpectedly useful with the  
15           biodegradable polyesters of the present invention.

          The biodegradable polyester may be for example, polylactic acid, polycaprolactone, polyethylene succinate, polypropylene succinate, polybutylene succinate, polyhydroxyalkanoate (PHA), for example  
20           polyhydroxybutyrate (PHB) or copolymers of hydroxybutyrate with hydroxyvalerate, i.e. polyhydroxybutyrate-co-hydroxyvalerate, (PHBV). It may be for example a poly-2-hydroxyalkanoate such as a polyglycolic acid or it may be a synthetic polypropiolactone, polybutyrolactone, polyvalerolactone, or a caprolactone copolymer.

25           Examples of suitable synthetic polyesters are especially polycaprolactone, polylactides, and polyesters containing combinations of dicarboxylic acids or derivatives thereof and diols. Dicarboxylic acids being selected from the group consisting of malonic, succinic, glutaric, adipic, pimelic, azelaic, sebacic, fumaric, 2,2-dimethylglutaric, suberic,  
30           1,3-cyclopentane dicarboxylic, 1,4-dicyclohexane-dicarboxylic, 1,3-cyclohexane dicarboxylic, diglycolic, itaconic, maleic, 2,5-norbornane dicarboxylic and ester forming derivatives thereof and combinations thereof, and diols selected from the group consisting of ethylene glycol, diethylene glycol, propylene glycol, 1,3-propanediol, 2,2-dimethyl-1,3-

propanediol, 1,3 butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2,2-trimethyl-1,6-hexanediol, thiodiethanol, 1,3-cyclohexanedimethanol, 1,4-cyclohexanedimethanol, 2,2,4,4-tetramethyl-1,3-cyclobutanediol, triethyleneglycol, tetraethyleneglycol, di-, tri-, tetra-propyleneglycol and combinations thereof, cellulose and cellulose esters such as acetates, propionates or butyrates, polypeptides, proteins and polyamides, copolymer of succinic acid and butylene glycol.

Examples of suitable polyesters are PHAs having units of formula I:



where m is in the range 1-13 and n is 2m or (if m is at least 2) 2m-2.

Typically  $C_m H_n$  contains 1-5 carbon atoms in the polymer chain and the remainder (if any) in a side chain. In very suitable polyesters n is 2m and especially there are units with  $m = 3$  and  $m = 4$  copolymerised together and with respectively a  $C_1$  and  $C_2$  side chain on the carbon next to oxygen in the chain. Particular polyesters contain a preponderance of  $m = 3$  units, for example, homopolymer of PHB, or copolymer (PHBV) especially with 70 - 98 mol % of such  $m = 3$  units, the balance (if any) being units in which  $m = 4$ . More preferably copolymers contain 4-20 mol% of  $m = 4$  units. The molecular weight of the PHA is preferably over 50000, especially over 300000.

The PHA may also be a blend of two or more copolymers differing in their relative values of m. An example contains

- (a) PHA consisting essentially of Formula I units in which 2-5 mol% of units have  $m = 4$ , the rest  $m = 3$ ; and
- (b) PHA consisting essentially of Formula I units in which 5-30 mol% of units have  $m = 4$ , the rest  $m = 3$ .

In each such PHA there are side chains as above mentioned. The proportions in such a blend are preferably such as give an average  $m = 4$  content in the range 4 - 18 mol %.

In each such PHA having units with  $m = 3$  and  $m = 4$  there may be very small, typically fractional, percentages of units having higher values of m. PHA consisting essentially of  $m = 3$  units is polyhydroxybutyrate (PHB), and PHA consisting of  $m = 3$  and 4 units is

polyhydroxybutyrate-co-valerate (PHBV).

The polyhydroxyalkanoate is preferably PHB or PHBV, which may be 3-hydroxy or 4-hydroxy or a mixture of both. Especially preferred are the (R)-3-hydroxy forms of PHB and PHBV.

5        The composition may contain a blend of biodegradable polyesters. In particular in such compositions, a blend of at least 50% w/w of PHA is preferred with another polymer, particularly those mentioned above. Blends of particular interest are blends of PHA with polycaprolactone, polylactic acid, and cellulose esters and up to 50% w/w of the blend  
10        preferably comprises one or more polymers selected from polycaprolactone, polylactic acid and cellulose esters, particularly PHBV and polycaprolactone and PHBV and cellulose esters.

      The PHA is preferably a fermentation product, especially of a microbiological process in which a microorganism lays down PHA during  
15        normal growth or is caused to do so by cultivation in the absence of one or more nutrients necessary for cell multiplication. The microorganism may be wild or mutated or may have had the necessary genetic material introduced into it. Alternatively the necessary genetic material may be harboured by a eukariote, to effect the microbiological process.

20        A suitable microbiological process is described in for Formula I material with  $m=3$  or  $m =$  partly 3, partly 4 : EP-A-69497 (Alcaligenes eutrophus);  
      for Formula I materials with  $m = 3$ :  
      US 4101533 (Alcaligenes eutrophus H-16)  
25        EP-A-144017 (Alcaligenes latus);  
      for Formula I material with  $m = 7-13$   
      EP-A-0392687 (various Pseudomonas)

      The PHA can be extracted from the fermentation product cells by means of an organic solvent, or the cellular protein material may be  
30        decomposed leaving microscopic granules of polymer. For specialised end uses the cellular protein may be partly or wholly allowed to remain with the PHA, but preferably subjected to cell breakage.

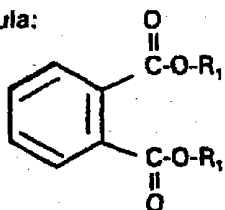
      Alternately, the PHA can be a product of synthetic chemistry. PHB can be made by the method of Bloembergen and Holden,

Macromolecules 1989, Vol 22, p1656-p1663. PHBV can be made by the method of Bloembergen, Holden, Bluhm, Haymer and Marchessault, Macromolecules 1989, Vol 22, p1663-1669).

The plasticiser is a material capable of plasticising polyester, i.e. capable of improving the ductility of the polyester and especially a material capable of plasticising PHB or PHBV. There may be one or more plasticisers present. For the ratio of such plasticiser to biodegradable polyester, the range up to 40 phr w/w (particularly 1 to 40 phr w/w) includes most of the likely uses and, for making effectively rigid but not brittle articles, the range 5-25 phr w/w is generally suitable.

Examples of suitable plasticisers are

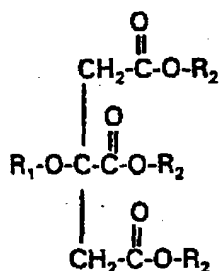
- (A) high-boiling esters of polybasic acids, such as  
(i) phthalates and isophthalates, particularly compounds of the formula:



where R<sub>1</sub> is C<sub>1-20</sub> alkyl, cycloalkyl or benzyl, preferably C<sub>5-11</sub> alkyl, cyclohexyl or benzyl, especially isoheptyl, isoocetyl, isononyl, isodecyl and isoundecyl. For example di-isodecylphthalate (Jayflex DIDP\*), di-isooctylphthalate (Jayflex DIOP\*), di-isoheptylphthalate (Jayflex77(DHIP)\*), di-baptylphthalate, di-rindecylphthalate, di-isononylphthalate (Jayflex DNIP\*), di-isoundecylphthalate (Jayflex DIUP\*), di-isodecylphthalate (Reomol DiDP\*), di-isobutylphthalate (Reomol DiBP\*) di-tridecylphthalate, butyl benzyl phthalate (Ketjenflex 160\*);

- (ii) citrates; International Patent Application No. PCT/GB 93/01689 discloses a range of doubly esterified hydroxycarboxylic acids having at least 3 ester groups in its molecule. A particularly preferred example from that disclosure is acetyl tri-n-butyl citrate (Estaflex\*). Further citrates of the formula :

5



where  $R_1$  is hydrogen or  $C_{1-10}$  alkyl, and  $R_2$  is  $C_{1-10}$  alkyl,  $C_{1-10}$  alkoxy or  $C_{1-10}$  alkoxyalkyl. When  $R_1$  and  $R_2$  are alkyl each is preferably selected from straight or branched chain, methyl, ethyl, propyl, butyl, pentyl, hexyl, iso-propyl, isobutyl, or ethoxy, propoxy, butyoxo, butoxyethyl, butoxy-isopropyl and butoxyethoxy are encompassed by the present invention.

10

Particular examples are : triethylcitrate, trimethylcitrate, n-butyl tri-n-hexylcitrate (Citroflex B6), tri-n-butylcitrate (Citroflex 4).

15

(v) fumarates;

(vi) glutamates such as diester ether alkyl (Plasthall 7050');;

(vii) adipates, such as those of the formula  $R_1 - O - C(O) - (CH_2)_4 - C(O) - OR_2$ , where  $R_1$  and  $R_2$  which may be the same or different are  $C_{2-12}$  alkyl (e.g. butyl),  $C_{2-12}$  alkoxy (e.g. butoxyethoxy),  $C_{2-12}$  alkoxyalkyl (e.g. butoxyethyl), for example, di-2-ethylhexyl adipate (Reomol DOA'), di-isodecyl adipate, di-isononyl adipate, dioctyl adipate; The esterified radicals may be for example  $C_1 - C_{12}$  alkyl, aryl, aralkyl or aralkyl.

20

(viii) Sebacic acid derivatives of the formula  $R_1 - O - C(O) - (CH_2)_8 - C(O) - O - R_2$ , where  $R_1$  is  $C_{2-15}$  alkyl or  $C_{2-15}$  alkoxyalkyl, for example, di-octyl sebacate, di-dodecyl sebacate, di-butoxyethyl sebacate, or di-n-butyl sebacate;

25

(ix) Azelaic acid derivatives of the formula  $R_1 - O - C(O) - (CH_2)_7 - C(O) - R_2$ , where  $R_1$  is  $C_{2-12}$  alkyl, benzyl, or  $C_{2-12}$  alkoxy-alkyl, for example, di-n-butyl azelate and di-i-octyl azelate;

30

(B) high-boiling glycols, polyglycols, polyoxyalkylenes and glycerol each optionally substituted and optionally terminally esterified:

(i) high molecular weight glycols such as triethylene glyc I diacetate (Estol 1593'), triethylene glycol caprylate (Plasthall 4141'), alkyl



ethers/esters of general formula  $R_2-(O-CH_2-CH_2-O-CH_2-CH_2-O)_n-R_1$  (optionally the repeating ethoxy can be isopropoxy) where  $n$  is 2 or more, for example Morton TP90B<sup>\*</sup> where  $R_2$  is  $C_4H_9-$  and  $n$  is 2, Reomol BCF where  $R_1$  is  $-C(O)-alkyl$ ,  $R_2$  is  $C_4H_9-$  and  $n$  is 2, Reomol BCD where  $R_1$  is  $-C(O)-alkyl$ ,  $R_2$  is  $C_4H_9-$  and  $n$  is 2, Morton TP759<sup>\*</sup>, compounds of such formula where  $R_1$  is  $-C(O)-C_mH_{2m+1}$  particularly up to  $m=20$ , e.g. lauryl when  $m$  is 12, palmitate when  $m$  is 15 or oleate when  $m$  is 15 and unsaturated, stearyl when  $n$  is 17,  $R_2$  is sorbitan and  $n$  is up to 20, for example Tween 80 in which  $R_2$  is sorbitan monooleate,  $R_1$  is lauryl and  $n$  is 20; and such compounds containing irregularly spaced ether linkages, for example the compounds of the formula above in which  $R_1$  is hydrogen,  $R_2$  is alkylphenyl where the alkyl is  $C_{2-12}$  alkyl, and  $n$  is 2 to 100, for example, Igepal CA210<sup>\*</sup> where the alkyl is  $C_8$  alkyl and  $n$  is 2, Igepal CA510<sup>\*</sup> which is the same as CA210 except that  $n$  is 5, Triton X-100<sup>\*</sup> and Triton X-405<sup>\*</sup> which is the same as Igepal CA510<sup>\*</sup> except that  $n$  is 10 and 40 respectively, Plasthall CPH27N, CPH30N and CPH39 where  $R_1$  is hydrogen,  $R_2$  is  $CH_3-(CH_2)_{10}-C(O)-$  and  $n$  is 10, 5 and 15 respectively, Plasthall CPH39N and CPH41N in which  $R_1$  is hydrogen,  $R_2$  is  $CH_3-(CH_2)_7-CH=CH-(CH_2)_7-C(O)-$  and  $n$  is 5 and 15 respectively; PEG 2000, PEG 6000 and PEG 10000 where  $R_1$  and  $R_2$  are both hydrogen and  $n$  is 50, 150 and 200 respectively;

(ii) examples of polyglycols are poly(propylene glycol) (PPG 100<sup>\*</sup>, PPG 725<sup>\*</sup>, PPG 425<sup>\*</sup>), poly(ethylene glycol) (PEG 300<sup>\*</sup>, PEG 200<sup>\*</sup>);

(iii) examples of glycerol derivatives are glycerol tricaprolate, glycerol tributyrate;

(iv) pentaerythritols and derivatives;

The acid-derived radical of the ester typically contains 2-10 carbon atoms.

(C) sulphonic acid derivatives such as toluenesulphonamide (Ketjenflex 15<sup>\*</sup>, Ketjenflex 8<sup>\*</sup>, Ketjenflex 7<sup>\*</sup>, Ketjenflex 3<sup>\*</sup>);

(D) epoxy derivatives such as the compounds of formula  $CH_3-(CH_2)_n-$

- A-(CH<sub>2</sub>)<sub>n</sub>-R in which the A is an alkene containing one or more double bonds (i.e. unsaturated fatty acids), n is up to 25 and R is C<sub>2-15</sub> alkyl, epoxidised esters of fatty acids, epoxidised soya bean oil, epoxidised linseed oils, epoxidised octyl tallate, epoxidised glycololeate, e.g. Lankro EDG<sup>\*</sup>, Lankro GE<sup>\*</sup>, Paraplex G60<sup>\*</sup>, Paraplex G62<sup>\*</sup>, Plasthall E50<sup>\*</sup>, Rheoplas 39<sup>\*</sup> and Lankro L<sup>\*</sup>;
- (E) substituted fatty acids such as palmitates, stearates, oleates, ricinoleates and laurates, for example, sorbitan monolaurate, sorbitan monooleate, poly(oxyethylene)(20)Sorbitan monolaurate (Tween 20<sup>\*</sup>), poly(oxyethylene)(4)lauryl ether (Brij 30<sup>\*</sup>), butyl acetyl ricinoleate (BAR<sup>\*</sup>);
- (F) phosphoric acid derivatives (phosphates), particularly compounds of the formula O=P(OR)<sub>3</sub> where R is alkyl, alkoxyalkyl, phenyl or phenylalkyl for example, isopropyl-phenyl. Particular examples are: phosphate ester (Reomol 249<sup>\*</sup>), tri-isopropyl phenyl phosphate (Reofos 95<sup>\*</sup>); and phosphonic acid derivatives and phosphites;
- (G) chlorinated paraffins such as Cereclor 56L<sup>\*</sup>, Cerechlor 552;
- (H) polymeric esters such as those of the formula -O-C(O)-R<sub>1</sub>-C(O)-O-R<sub>2</sub>-O- in which R<sub>1</sub> and R<sub>2</sub> are both independently C<sub>2-12</sub> alkyl, or R<sub>2</sub> may be derived from a diol such as 1,2-propanediol, 1,3-butanediol, 1,4-butanediol or 1,6-hexanediol; for example;
- (i) glutaric polyesters (polyester glutarates) having molecular weights from 2000 to 20,000, e.g. Plasthall 550<sup>\*</sup>, Plasthall 7046<sup>\*</sup>, Plasthall 7092<sup>\*</sup> Paraplex P550<sup>\*</sup>, Paraplex P7035<sup>\*</sup>;
- (ii) adipic polyesters (polyester adipates) having a molecular weight from 200 to 20000, for example, Plasthall 643<sup>\*</sup>, Plasthall 650<sup>\*</sup>, poly(propylene) adipate for example LANKROFLEX PLA<sup>\*</sup>, LANKROFLEX PPL<sup>\*</sup>, LANKROFLEX PPA/3<sup>\*</sup>, Paraplex G56<sup>\*</sup>, Paraplex G59<sup>\*</sup>, Diolpate 214<sup>\*</sup>, Diolpate 917<sup>\*</sup>;
- (iii) succinic polyesters;
- (iv) sebacic polyesters (polyester sebacate) having a molecular weight from 4000 to 10000, preferably 8000, for example, Plasthall 1070<sup>\*</sup>;

- (iv) Diolpate OL1696\*, Diorex 570\*;
- (v) lactone copolymers of the formula  $[-(O-C(O)-R_1-C(O)-O)-(R_2-O)]_m-[(C(O)-R_3-O)]_n$ , where  $R_1$  and  $R_2$  are both independently  $C_{2-12}$  alkyl, or  $R_2$  may be derived from a diol such as 1,2-propanediol, 1,3-butanediol, 1,4-butanediol or 1,6-hexanediol, and  $R_3$  is  $-(CH_2)_6-$  (based on caprolactone);
- (vi) polyesters such as Reoplex 346\*, Reoplex 1102\*, Reomol MD (ester of mixed adipic, glutaric and succinic acids with isodecanol), polycaprolactone triol (PCL Triol (300)\*);
- (J) Wolflex-But\*;

Generally it is preferred that the plasticiser should be biodegradable.

Preferred plasticisers are the polymeric esters, high-boiling glycols, polyglycols, polyoxyalkylenes and glycerol each optionally substituted and optionally terminally esterified, epoxidised soyabean oils, adipates, sebacates, phosphate esters, phthalates, citrates, castor oil, chlorinated paraffins and toluene sulphonamide derivatives.

Particularly preferred are epoxidised natural oils, phthalate derivatives, polypropylene adipates, phosphoric acid derivatives, polymeric esters. Especially polypropylene glycol adipate, substituted polyethylene glycol, polyester glutarate and epoxidised soyabean oil.

Plasticisers which are particularly preferred for conferring improved impact properties are high molecular weight glycols of general formula  $R_2-(O-CH_2-CH_2-O-CH_2-CH_2-O)_n-R_1$ , for example Reomol BCD, adipates, for example di-isodecyl adipate, mixed polyesters, for example Reomol MD, polyester glutarate, for example Paraplex 550, and citrates.

In a further aspect of the invention the polyester composition may contain at least two plasticisers selected from those defined herein. In a yet further aspect of the present invention the polyester composition may contain one or more plasticisers selected from those defined herein and may additionally contain one or more plasticisers previously known to plasticise polyhydroxyalkanoates, for example, citrates containing doubly esterified hydroxycarboxylic acids having at least 3 ester groups in the molecule, glycerol triacetate and glycerol diacetate. Of particular interest

is a polyester composition containing as plasticisers acetyl tri-n-butyl citrate (Estaflex<sup>®</sup>) and any of the plasticisers defined herein, especially acetyl tri-n-butyl citrate (Estaflex<sup>®</sup>) and epoxidised soya bean oil.

5 The invention further provides for the use of any of the plasticisers defined above for plasticising a biodegradable polyester composition as defined above.

The composition can contain the usual polymer processing additives such as fillers, fibres, nucleants, for example boron nitride, and pigments such as titanium dioxide. It can be in the form of mouldings,  
10 extrudates, coatings, films or fibres, including multilayer coatings, films or fibres. The nucleant is generally present in amounts from 0.1 phr to 10 phr w/w, preferably 1 to 5 phr w/w.

The invention provides methods of making the composition by mixing its components. If desired, this may be effected in a solvent,  
15 such as a halogenated hydrocarbon or alkylene carbonate. Such a method is convenient for coating or for centrifugal spinning of fibres. More conveniently, the plasticiser is mixed with powdered dry polymer and the mixture is treated in conditions of shear, such as in a plastic mill or extruder. The product is then granulated and used as feed for a  
20 shaping operation such as extrusion, injection moulding, injection blow-moulding or compression moulding.

The composition is especially useful for making the following shaped articles: films, especially for packaging, fibres, non-woven fabrics, extruded nets, personal hygiene products, bottles and drinking vessels,  
25 agricultural and horticultural films and vessels, ostomy bags, coated products (such as paper, paperboard, non-woven fabrics), agricultural and horticultural films and vessels, slow-release devices. Alternatively, the polymer composition with suitable additives can be used as an adhesive.

The invention is now further described, but is not limited by, the  
30 following examples. In the following examples the tests were conducted with PHBV of the (R)-3-hydroxy form.

#### Example 1

Compositions were prepared by mixing PHBV copolymer (10% HV) (500 g) with 1 phr boron nitride (as nucleant) and 20 phr of

plasticiser. The mixture was extruded in a Betol 2520 extruder under these conditions: Zone 1 = 130°C; Zone 2 = 140°C; Zone 3 = 150°C; Die = 150°C; Screw Speed = 100 rpm.

5 The extrudate, a single 4mm lace, was crystallised at 50-60°C in a water bath, dried in a current of air and cut into granules.

The granules were then injection moulded (Boy 15S) into tensile bars, dumbbell shaped according to ISO R 537/2, their prismatic part measuring 40 x 5 x 2 mm. The bars were numbered as they came out of the mould, then allowed to cool at ambient temperature.

10 Injection moulding conditions were: Barrel Zone 1 = 130°C; Barrel Zone 2 = 130°C; Nozzle = 130°C; Mould heater temperature = 74-77°C; Mould temperature = 60°C; Pressure hold on time = 12 sec; Cooling time = 30 sec; Injection pressure 45 bar; Screw speed = 250 rpm.

15 Tensile testing was carried out using an Instron 1122 fitted with a Nene data analysis system. The jaw separation used was 50 mm and crosshead speed was 10 mm/min<sup>-1</sup>. The samples were measured after 30 days for elongation at break. The results are presented in Table 1 in percentage elongation to break (E%) relative to the starting gauge length of 40mm.

#### Glass transition temperature (T<sub>g</sub>) measurement

20 The blends were prepared by dispersing the plasticiser (20 phr) onto 10g of PHBV copolymer (10% HV). The plasticiser was dissolved in 20-25ml methanol (or chloroform if immiscible with methanol) and the polymer powder fully wetted. The solvent was allowed to evaporate off at room temperature for 3-4 hours before the blend was finally dried at 60°C for 30 minutes.

25 The T<sub>g</sub> measurement was carried out by differential scanning calorimetry (DSC) analysis using a Perkin Elmer DSC7 under a nitrogen atmosphere. 10mg samples were used in the following temperature regime : melt sample at 200°C for 2 minutes, cool rapidly to -80°C and hold at this temperature until the system has equilibrated. Heat at 20°C min<sup>-1</sup> from -80°C to 50°C. The T<sub>g</sub> was reported as the point of inflection (in the trace) for the second heating step.

Table 1

	Plasticiser	T <sub>g</sub> /°C	E (%)
	No plasticiser	0	8.5
	poly(ethylene glycol) (PEG 200)	-19.5	10
5	poly(ethylene glycol) (PEG 300)	-20.5	11.75
	poly(propylene glycol) (PPG 1000)	-10.19	12.75
	ditridecyl phthalate	-10.92	12.75
	poly(oxyethylene)(4)lauryl ether (Brij 30)	-9.3	13.75
10	poly(oxyethylene)(20)sorbitan monolaurate (Tween 20)	-16.6	14
	di-isoundecylphthalate (Jayflex DIUP)	-8.38	14.5
	polycaprolactone triol (PCL (Mw 300)	-8.3	15.75
	poly(propylene glycol) (PPG 425)	-23.13	16.75
15	di-isononylphthalate (Jayflex DINP)	-12.77	16.75
	di-isooheptylphthalate (Jayflex 77 DIHP)	-19.42	20
	poly(propylene glycol) (PPG 725)	-14.2	21.5
	di-iso-octylphthalate (Jayflex DIOP)	-15.84	22
	di-isodecylphthalate (Jayflex DIDP)	-10.06	22.5
20	epoxidised soya bean oil (Reoplast 39)	-9.5	34.25

The plasticisers used in this example are available from commercial suppliers (BDH, Aldrich Chemicals, Exxon Chemicals, and Ciba Geigy).

#### Example 2

25 Compositions were prepared by mixing PHBV copolymer (11% HV) (500 g) with 1 phr boron nitride (as nucleant) and 100g (20 phr) of

plasticiser. The mixture was extruded in a Betol 2520 extruder under these conditions: Zone 1 = 115°C; Zone 2 = 133°C; Zone 3 = 153°C; Die = 158°C = Screw Speed = 100 rpm.

5 The extrudate, a single 4mm lace, was crystallised at 50-60°C in a water bath, dried overnight at a low temperature (40°C) and cut into granules.

The granules were then injection moulded (Boy 15S) into tensile bars, dumbbell shaped according to ISO R 537/2, their prismatic part measuring 40 x 5 x 2 mm. The bars were numbered as they came out of the mould.

10 Injection moulding conditions were: Barrel Zone 1 = 130°C; Barrel Zone 2 = 130°C; Nozzle = 134°C; Mould heater temperature = 74-77°C; Mould temperature = 60°C; Pressure hold on time = 12 sec; Cooling time = 12 sec; Injection pressure = 45 bar; Screw speed = 250 rpm.

15 Tensile testing was carried out using an Instron 1122 fitted with a Nene data analysis system. The jaw separation used was 50 mm and crosshead speed was 10 mm/min<sup>-1</sup>. The samples were measured after 90 days for elongation at break. The results are presented in Table 2 as percentage elongation to break relative to the starting gauge length of 40 mm.

20 The T<sub>g</sub> tests of this example were carried out on samples taken from the extruded lace. The DSC analysis was conducted as in Example 1 except for the following conditions: sample size = 7-10 mg; sample cooled rapidly to -50°C at 100°C min<sup>-1</sup>; allowed to equilibrate at -50°C; heated at 20°C min<sup>-1</sup> to 205°C.

25 The plasticisers used in this example are available from commercial suppliers (Unichema International, Akzo Chemie, FMC Corporation, C.P. Hall, ICI, Kemira Polymers).

Table 2

	Plasticiser	T <sub>g</sub> /°C	E (%)
	No plasticiser	0.8	13.5
	D-A Sebacate	-8.7	16.5
5	glycerol diacetate (Estol 1582)	-12.9	19.5
	toluene sulphonamide (Ketjenflex 3)	-8.6	21.8
	toluene sulphonamide (Ketjenflex 7)	-10.2	24
	di-2-ethylhexyl adipate (Reomol DOA)	-10.7	26.5
	butyl acetyl ricinoleate (BAR)	-8.5	28.3
10	di-isobutylphthalate (Reomol DiBP)	-16	28.5
	diester ether alkyl (Plashall 7050)	-26.3	29.3
	toluene sulphonamide (Ketjenflex 8)	-7.8	29.3
	triethylene glycol diacetate (Estol 1593)	-28	32
	triethylene glycol caprylate (Plasthall 4141)	-24	34
15	alkyl aryl phosphate (Ketjenflex 141)	-17.8	34.5
	toluene sulphonamide (Ketjenflex 15)	-7.4	38
	chlorinated paraffin (Cereclor 56L)	-7.2	41.5
	polyester (Reoplex 346)	-16.4	42.3
	di-isodecylphthalate (Reomol DiDP)	-6.6	43.8
20	adipic polyester (Plasthall 643)	-11.4	45
	butyl benzyl phthalate (Ketjenflex 160)	-13.8	45.3
	chlorinated paraffin (Cerechlor 552)	-11.8	51.5
	Wolflex-But	-9.8	52.8
	glutaric polyester (Plasthall 550)	-7.8	52.8



p lyester (R oplex 1102)	-13.5	53.5
polymeric ester (Diorex 570)	-14	54.3
polymeric ester (Diolpate OL1696)	-15	54.8
tri-isopropyl phenyl phosphate (Reofos 95)	-9.2	55.3
phosphate ester (Reomol 249)	-17.3	60.8

**Example 3**

Compositions were prepared by mixing PHBV copolymer (6.6% HV, Mw of 680,000) with 1 phr boron nitride (as nucleant) and 20 phr of plasticiser. The mixture was blended for 10 minutes then extruded in a Betol 2520 extruder under the following conditions:

Zone 1 = non-plasticised 140°C; plasticised 130°C;

Zone 2 = non-plasticised 150°C; plasticised 140°;

Zone 3 = non-plasticised 160°C; plasticised 140°C;

Die = non-plasticised 160°C; plasticised 150°C;

The extrudate, a single 4mm lace, was crystallised at 50-60°C in a water bath, dried overnight at a low temperature (40°C) and cut into granules.

The granules were then injection moulded (Boy 305) into tensile bars, dumbbell shaped according to ISO R 537/2, their prismatic part measuring 40 x 5 x 2 mm. The bars were numbered as they came out of the mould.

Injection moulding conditions were:-

Zones 1 to 3 temperature = as for the extrusion process ;

Injection time = 16 seconds;

Nozzle temperature = 150°C;

Mould heater temperature = 60-70°C;

Mould temperature = 60°C;

Pressure hold on time = 16 sec;

Cooling time = 16 sec;

Screw speed = 240 rpm.

Tensile testing was carried out using an Instron 4501 instrument system. The jaw separation used was 50 mm and crosshead speed was 10 mm/min<sup>-1</sup>. The samples were measured after 30 days for elongation at break. The results are presented in Table 3 as percentage elongation to break relative to a starting gauge length of 40mm.

The  $T_g$  tests of this example were carried out on samples from the injection moulded test pieces. The DSC analysis was conducted as in Example 1 except for the following conditions: sample size = 7-10 mg; sample cooled rapidly to -80°C at 100°C min<sup>-1</sup>; allowed to equilibrate at -80°C; heated at 20°C min<sup>-1</sup> to 200°C.

The results are presented in Table 3 as percentage elongation to break relative to a starting gauge length of 40mm.

Impact testing was carried out on a notched impact test piece of 11.8mm x 1.3mm x 4mm using a Zwick Izod impact tester at 28°C. The results are presented in Table 3. Where a  $T_g$  is available for the material this is placed alongside the result in the Table.

Table 3

Plasticiser	%E	$T_g$	Plasticiser	IZOD	$T_g$
None	15.4		None	70.8	
1	15.4		5	71	
2	18.5		53	98.8	
3	16.7		44	104	
4	17.0		4	105	
5	17.4		18	107.8	-8.3
6	17.7	-11.9	38	110	
7	18.9		41	110.3	1.39
8	18.9		17	111.3	
9	19.1	-13.5	26	111.8	

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Plasticiser	%E	T <sub>g</sub>	Plasticiser	IZOD	T <sub>g</sub>
10	20.4		56	112	
11	20.5	-19.6	23	117	
12	21.3		15	125	
13	22	-12.7	50	125.3	
14	22.1	-18.6	1	127.1	
15	23.1		17	128	
16	23.3		64	129.8	-22.8
17	24.2		65	130.3	-10.5
18	24.6	-8.3	10	130.3	
19	24.7	-12.6	66	135	-7.5
20	25	-8.5	3	136.8	
21	25		32	138	
22	25		21	142.8	
23	25.2		60	144.8	
24	25.6	-4.2	48	149.8	-3.67
25	26.1	-3.8	52	152	
26	26.2		47	155.8	
27	26.8	-25.3	7	155.8	
28	27.8	-22.8	40	159	
29	29.4	-21.5	36	160.8	
30	29.6	-18.5	34	164.3	-6.5
31	29.6	-6.1	51	164.8	

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Plasticiser	%E	T <sub>g</sub>	Plasticiser	IZOD	T <sub>g</sub>
32	30.2		63	166.3	-3.5
33	30.3	-17.9	49	166.8	-15.8
34	30.8	-6.5	58	166.8	
35	31.1		43	167.3	
36	31.3		16	167.8	
37	31.3	-18.3	6	169.4	-11.9
38	31.7		29	170.8	-21.5
39	33.3	-26.2	62	182.3	-6.6
40	34.2		33	183.3	-17.9
41	34.3	-1.4	56	185	
42	34.4	-22.0	13	186.6	-12.7
43	35.3	-10.8	45	187.3	-6.3
44	35.4		31	192.8	-6.1
45	36	-6.3	2	195.4	
46	36.4	-2.1	67	197.5	-3.1
47	38.5		19	197.8	-12.6
48	38.6	-3.7	61	197.8	
49	39	-15.8	59	198.8	-13
50	40.5		57	200.8	-4.2
51	40.6		68	201.8	-25.3
52	42.9		14	202.8	-18.6
53	47.6		35	204.8	

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Plasticiser	%E	T <sub>g</sub>	Plasticiser	IZOD	T <sub>g</sub>
54	48.4	-14.5	25	215.8	-3.8
55	48.4	-1.2	9	220.8	-13.5
56	48.6		37	227.3	-18.3
57	55.7	-4.2	38	227.8	
58	59.3		42	228.3	-22
59	60.7	-13.0	39	231.8	-26.2
60	68.9		11	235.6	-19.6
61	82.3		55	241	-1.2
62	96.6	-6.56	20	243.3	-8.5
63	162.7	-3.49	30	251.8	-18.5
			69	257.8	-1.5
			54	271.3	-14.5
			22	273.8	
			46	301.3	-2.1
			12	265.8	

Key

- 1 1,4-butane diol adipic acid (S102250) available from Occidental Chemical
- 2 1,4-butane diol adipic acid (S102250) (35phr)
- 3 polyethylene glycol 2000 available from Aldrich Chemical
- 4 polycaprolactone (Tone 301) available from Union Carbide
- 5 polyethylene glycol 6000 available from Aldrich Chemical
- 6 Triton X100 (polyethoxyethanol) available from Aldrich Chemical
- 7 1,4-butane diol adipic acid (S1063210) available from Occidental Chemical

- 8 neopentylglycol-adipic acid-caprolactone (S1063210) available from Occidental Chemical
- 9 triethylcitrate (Citroflex 2) available from Morflex Inc.
- 10 polyester adipate (MW = 2000) (Plasthall P643) available from C.P. Hall
- 5 11 Morton TP95 (polyether) available from Morton Thiokol Inc
- 12 di-isononyladipate (Jayflex DINA2) available from Exxon Chemical
- 13 Reomol 249 (phosphate ester) available from FMC Corporation
- 14 Monoplex 573 (epoxidised octyl tallate) available from C.P. Hall
- 10 15 PEG 600 monolaurate (Plasthall CPH43N) available from C.P. Hall
- 16 Epoxidised soyabean oil (Plasthall ESO) available from C.P. Hall
- 17 PEG 200 Monolaurate (Plasthall CPH27N) available from available from C.P. Hall
- 18 Epoxidised soya bean oil (Paraplex G60) available from C.P. Hall
- 15 19 acetyl tri-n-butyl citrate (Citroflex A4) available from Morflex Inc
- 20 acetyl triethyl citrate (Citroflex A2) available from Morflex Inc
- 21 polyester sebecate (Plasthall P1070) available from C.P. Hall
- 22 neopentylglycol-adipic acid-caprolactone (S1063210) (35phr) available from Occidental Chemical
- 20 23 F1040250 trifunctional polyester adipates available from Occidental Chemical
- 24 polypropylene glycol adipate (low MW) (Lankroflex PPL) available from Harcros Chemicals
- 25 25 di isooctylazelate (Reomol DIOZ) available from FMC Corporation
- 26 polyester adipate (MW = 1200) (Plasthall P650) available from C.P. Hall
- 27 Butyl carbitol ether/ester (Reomol BCF) available from FMC Corporation
- 28 epoxidised linseed oil (Lankroflex L) available from Harcros Chemicals
- 29 epoxidised ester of fatty acid (Lankroflex ED6) available from Harcros Chemicals
- 30 30 tri-n-butylcitrate (Citroflex 4) available from Morflex Inc
- 31 epoxidised soyabean oil (Paraplex G62) available from C.P. Hall
- 32 p lyoxyethylene laurate (Plasthall CPH 376N) available from C.P. Hall
- 33 Morton TP759 available from Morton Thiokol

- 34 dioctyladipate (Jayflex DOA2) available from Exxon Chemical
- 35 polyester glutarate (Plasthall P7092) available from C.P. Hall
- 36 polyester adipate (Diolpate 917) available from Kemira Chemical
- 37 butyl carbitol ether/ester (Reomol BCD) available from FMC Corporation
- 38 octylphenyl substituted PEG (Igepal CA520)
- 39 Morton TP90B available from Morton Thiokol
- 40 trifunctional polyester adipates (F1040250) (35phr) available from Occidental Chemical
- 41 epoxidised soya bean oil (Lankroflex GE) available from Harcros Chemical
- 42 acetyltributylcitrate (Estaflex\*) available from Akzo Chemie
- 43 acetyltrimethylcitrate available from Morflex Inc
- 44 PEG 600 monooleate (Plasthall CPH41N) available from C.P. Hall
- 45 butyl-tri-n-hexyl citrate (Citroflex B6) available from Morflex Inc
- 46 di-isodecyladipate (Jayflex DIDA2) available from Exxon Chemical
- 47 polyester adipate (Diolpate 214) available from Kemira Polymers
- 48 epoxidised soya bean oil (Reoplas 39) available from Ciba Geigy
- 49 di-n-butyl sebecate (Reomol DBS) available from Ciba Geigy
- 50 polyester adipate (MW = 4200) (Diolpate 214) available from Kemira Polymers
- 51 epoxidised glycol oleate (Monoplex S75) available from C.P. Hall
- 52 PEG 400 Monolaurate (Plasthall CPH30N) available from C.P. Hall
- 53 Castor oil available from Aldrich Chemical
- 54 Estaflex\*/epoxidised soyabean oil (Reoplas 39) (50/50) available from Akzo Chemie/Ciba Geigy
- 55 polyester glutarate (Paraplex P550) available from C.P. Hall
- 56 S1069285 (35phr) available from Occidental Chemical
- 57 PPG phthalate/adipate blend (Lankroflex 828) available from Harcros Chemical
- 58 polyester adipate (Paraplex G59) available from C.P. Hall
- 59 tri-isopropyl phenyl phosphate (Reofos 95) available from FMC Corporation
- 60 polypropylene adipate (Diolpate PPA350) available from Kemira

### Polymers

- 61 polyester glutarate (Plasthall P7035) available from C.P. Hall
- 62 PEG mono (1,1,3,3-tetramethylbutyl-phenyl ether (Igepal CA210)  
available from Aldrich Chemical
- 5 63 polypropyleneglycol adipate high MW (Lankroflex PPA3) available  
from Harcros Chemical
- 64 PEG 200 monooleate (Plasthall CPH27N) available from C.P. Hall
- 65 polyoxyethylene sorbitanmonolaurate (Tween 80) available from  
Aldrich Chemical
- 10 66 trimethylcitrate available from Morflex Inc
- 67 polyester glutarate (Plasthall P7046) available from C.P. Hall
- 68 butyl carbitol ether/ester (Reomol BCF) available from FMC  
Corporation
- 69 mixed polyester (Reomol MD) (ester of mixed adipic, glutaric and  
15 succinic acids with isodecanol) available from FMC Corporation

### Conclusions

All of the compounds evaluated as plasticisers in this example offer improved mechanical properties, and many of them demonstrated considerable improvements in elongation to break over the control which  
20 contained no processing additives. The most effective plasticiser was a polypropylene glycol adipate. A substituted polyethylene glycol (Igepal CA210) gave very good results as did some of the polyester glutarates. Phosphate esters, castor oil, epoxidised soya bean oils, epoxidised  
25 stearates, high boiling adipate and sebacate esters, citrates and a number of polyethylene glycol derivatives yielded elongations which were double that observed for the control. Blends of plasticisers were also effective. For example, a 50:50 blend of a citrate ester (Estaflex<sup>®</sup>) and an  
epoxidised soyabean oil gave superior results to when the plasticisers were used alone.

30 Traditional plasticiser theory predicts that the best plasticisers would yield the lowest  $T_g$ s. In this system, this is clearly not the case. For example, the most effective plasticiser in this study was Lankroflex PPA3. This gave an elongation to break of 162.7%. The  $T_g$  was only -3.5°C. By contrast Reomol BCF with a much lower  $T_g$  of -25.3°C gave a



much poorer elongation to break of 26.8%.

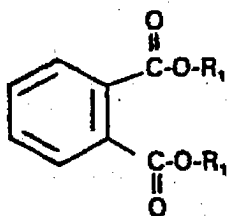
The Izod impact performance demonstrates a better correlation with  $T_g$ . Substituted PEGs such as Reomol BCD and the Morton range of plasticisers gave good results. Citrate esters were also highly effective.

## CLAIMS

1. Polyester composition comprising a biodegradable polyester and a plasticising quantity of at least one plasticiser selected from the group : high-boiling esters of polybasic acids; phosphoric acid derivatives; phosphorous acid derivatives; phosphonic acid derivatives; substituted fatty acids; high-boiling glycols, polyglycols, polyoxyalkylenes and glycerol each optionally substituted and optionally terminally esterified; pentaerythritols and derivatives; sulphonic acid derivatives; epoxy derivatives; chlorinated paraffins; polymeric esters; Wolflex-But<sup>®</sup>; provided that citrates does not include doubly esterified hydroxycarboxylic acids having at least 3 ester groups in its molecule and further provided that glycerols does not include glycerol triacetate and glycerol diacetate.
2. Polyester composition according to claim 1 wherein the biodegradable polyester is selected from the group: polylactic acid, polycaprolactone, polyethylene succinate, polypropylene succinate, polybutylene succinate, polypropiolactone, polybutyrolactone, polyvalerolactone, caprolactone copolymer, or polyhydroxyalkanoate.
3. Polyester composition according to claim 1 wherein the biodegradable polyester is selected from polyesters containing combinations of dicarboxylic acids or derivatives thereof and diols, the dicarboxylic acids being selected from the group consisting of malonic, succinic, glutaric, adipic, pimelic, azelaic, sebacic, fumaric, 2,2-dimethylglutaric, suberic, 1,3-cyclopentane dicarboxylic, 1,4-dicyclohexane-dicarboxylic, 1,3-cyclohexane dicarboxylic, diglycolic, itaconic, maleic, 2,5-norbornane dicarboxylic and ester forming derivatives thereof and combinations thereof, and diols selected from the group consisting of ethylene glycol, diethylene glycol, propylene glycol, 1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 1,3 butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2,2,4-trimethyl-1,6-hexanediol, 1,3-cyclohexanedimethanol, 1,4-

cyclohexanedimethanol, 2,2,4,4- tetramethyl-1,3-cyclobutanediol, triethyleneglycol, tetraethyleneglycol, di-, tri-, tetra-propyleneglycol and combinations thereof, cellulose and cellulose esters, polypeptides, proteins and polyamides, copolymer of succinic acid and butylene glycol.

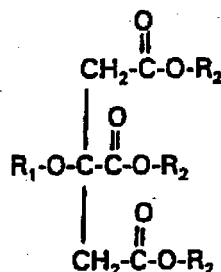
4. Polyester composition according to claim 1 or 2 wherein the polyhydroxyalkanoate is selected from polyhydroxybutyrate, polyhydroxybutyrate-co-hydroxyvalerate, polycaprolactone, polylactic acid or polyglycollic acid.
5. Polyester composition according to claim 4 wherein the polyhydroxyalkanoate is selected from poly-(R)-3-hydroxybutyrate and poly-(R)-3-hydroxybutyrate-co-(R)-3-hydroxyvalerate.
6. Polyester composition according to claim 1 wherein the high-boiling esters of polybasic acids are selected from the group comprising phthalates and isophthalates, citrates, fumarates, glutamates, adipates, sebacic acid derivatives and azelaic acid derivatives.
7. Polyester composition according to claim 6 wherein the phthalates and isophthalates are compounds of the formula:



where R<sub>1</sub> is C<sub>1-20</sub> alkyl, cycloalkyl or benzyl.

8. Polyester composition according to claim 1 wherein the phosphoric acid derivatives; phosphorous acid derivatives; phosphonic acid derivatives are selected from compounds of the formula  $O=P(OR)_3$ , where R is alkyl, alkoxyalkyl, phenyl or phenylalkyl,
9. Polyester composition according to claim 8 wherein the phosphoric acid derivative is a phosphate ester or tri-isopropyl phenyl phosphate.
10. Polyester composition according to claim 6 wherein the citrates

are selected from compounds of the formula :



where  $\text{R}_1$  is hydrogen or  $\text{C}_{1-10}$  alkyl, and  $\text{R}_2$  is  $\text{C}_{1-10}$  alkyl,  $\text{C}_{1-10}$  alkoxy or  $\text{C}_{1-10}$  alkoxyalkyl.

11. Polyester composition according to claim 1 wherein the substituted fatty acids are selected from palmitates, stearates, oleates, ricinoleates and laurates.
12. Polyester composition according to claim 11 wherein the substituted fatty acid is selected from sorbitan monolaurate, sorbitan monooleate, poly(oxyethylene)-(20)Sorbitan monolaurate, poly(oxyethylene)(4)lauryl ether and butyl acetyl ricinoleate.
13. Polyester composition according to claim 1 wherein the high-boiling glycols, polyglycols, polyoxyalkylenes and glycerol are selected from high molecular weight glycols, poly(propylene glycol), poly(ethylene) glycol, glycerol tricaprolate and glycerol tributyrate.
14. Polyester composition according to claim 13 wherein the high boiling glycols are selected from triethylene glycol diacetate, triethylene glycol caprylate, alkyl ethers/esters of general formula  $\text{R}_2-(\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{O})_n-\text{R}_1$  where  $n$  is 2 or more, where  $\text{R}_2$  is  $\text{C}_4\text{H}_9-$  and  $n$  is 2, or where  $\text{R}_1$  is  $-\text{O}-\text{alkyl}$ ,  $\text{R}_2$  is  $\text{C}_4\text{H}_9-$  and  $n$  is 2, or where  $\text{R}_1$  is  $-\text{C}(\text{O})-\text{alkyl}$ ,  $\text{R}_2$  is  $\text{C}_4\text{H}_9-$  and  $n$  is 2, compounds of such formula where  $\text{R}_1$  is  $-\text{C}(\text{O})-\text{C}_m\text{H}_{2m+1}$  and  $m$  is 1 to 20 optionally unsaturated and  $n$  is up to 20, and such compounds containing irregularly spaced ether linkages, for example the compounds of the formula above in which  $\text{R}_1$  hydrogen,  $\text{R}_2$  is alkylphenyl where the alkyl is  $\text{C}_{2-12}$  alkyl, (optionally the repeating thoxy may be isopropoxy) and  $n$  is 2 to 100.

15. Polyester composition according to claim 1 wherein the sulphonic acid derivative is a toluenesulphonamide.
16. Polyester composition according to claim 1 wherein the epoxy derivatives are selected from the compounds of formula  $\text{CH}_3-(\text{CH}_2)_n-\text{A}-(\text{CH}_2)_n-\text{R}$  in which the A is an alkene containing one or more double bonds, n is up to 25 and R is  $\text{C}_{2-18}$  alkyl, epoxidised esters of fatty acids, epoxidised soya bean oil, epoxidised linseed oils, epoxidised octyl tallate, epoxidised glycololeate.
17. Polyester composition according to claim 1 wherein the plasticiser is one or more chlorinated paraffins.
18. Polyester composition according to claim 1 wherein the polymeric esters are selected from compounds of the formula  $-\text{O}-\text{C}(\text{O})-\text{R}_1-\text{C}(\text{O})-\text{O}-\text{R}_2-\text{O}-$  in which  $\text{R}_1$  and  $\text{R}_2$  are both independently  $\text{C}_{2-12}$  alkyl, or  $\text{R}_2$  may be derived from a diol.
19. Polyester composition according to claim 18 wherein the polymeric ester is selected from glutaric polyesters having molecular weights from 2000 to 20,000, adipic polyesters having a molecular weight from 200 to 20,000, succinic polyesters, sebacic polyesters having a molecular weight from 4000 to 10,000, lactone copolymers of the formula  $[-(\text{O}-\text{C}(\text{O})-\text{R}_1-\text{C}(\text{O})-\text{O})-(\text{R}_2-\text{O})]_m-[(\text{C}(\text{O})-\text{R}_3-\text{O})]_n$  where  $\text{R}_1$  and  $\text{R}_2$  are both independently  $\text{C}_{2-12}$  alkyl, or  $\text{R}_2$  may be derived from a diol, and  $\text{R}_3$  is  $-(\text{CH}_2)_6-$  (based on caprolactone), polyesters of mixed adipic, glutaric and succinic acids, polycaprolactone triol
20. Polymer composition according to claim 1 wherein the plasticiser is selected from polymeric esters, high-boiling glycols, polyglycols, polyoxyalkylenes and glycerol each optionally substituted and optionally terminally esterified, epoxidised soyabean oils, adipates, sebacates, phosphate esters, phthalates, citrates, castor oil, chlorinated paraffins and toluene sulphonamide derivatives.
21. Polyester composition according to claim 20 wherein the plasticiser is selected from polypropylene glycol adipate, substituted polyethylene glycol, polyester glutarate and epoxidised soyabean oil.

22. Polyester composition according to claim 1 wherein the plasticiser is selected from high molecular weight glycols of general formula  $R_2-(O-CH_2-CH_2-O-CH_2-CH_2-O)_n-R_1$ , adipates, mixed polyesters, polyester glutarate and citrates.
23. Polyester composition according to any of the preceding claims which comprises a blend of two or more biodegradable polyesters in which at least 50% w/w is polyhydroxyalkanoate.
24. Polyester composition according to any of the preceding claims wherein up to 50% w/w of the blend comprises one or more polymers selected from polycaprolactone, polylactic acid and cellulose esters.
25. Polyester composition according to any of the preceding claims wherein the composition contains at least two plasticisers selected from any of those defined in any of the preceding claims.
26. Polyester composition according to any of the preceding claims wherein the composition contains one or more plasticisers selected from those defined in any of the preceding claims and additionally contains a plasticiser previously known to plasticise polyhydroxyalkanoates.
27. Polyester composition according to claim 26 wherein the composition additionally contains a plasticiser selected from citrates containing doubly esterified hydroxycarboxylic acids having at least 3 ester groups in the molecule, glycerol triacetate and glycerol diacetate.
28. Polyester composition according to claim 27 wherein the additional plasticiser is acetyl tri-n-butyl citrate.
29. Use of any of the plasticisers defined in any of claims 1 to 28 for plasticising a biodegradable polyester composition as defined in any of claims of claims 1 to 28.
30. Biodegradable polyester and a plasticising quantity of at least one plasticiser selected from the group : high-boiling esters of polybasic acids; citrates; phosphoric acid derivatives (phosphates); phosphonic acid derivatives; phosphites; substituted fatty acids; fumarates; glutamates; high-boiling glycols, polyglycols and

glycerol, optionally terminally esterified; pentaerythritols; sulphonic acid derivatives; epoxy derivatives including epoxidised natural oils; ricinoleates; adipates; chlorinated paraffins; polyesters including polycaprolactone triol; polymeric esters; glutaric polyesters; adipic polyesters; succinic polyesters; Wolflex-But<sup>®</sup>; provided that citrates does not include doubly esterified hydroxycarboxylic acids having at least 3 ester groups in its molecule and further provided that glycerols does not include glycerol triacetate and glycerol diacetate.

# INTERNATIONAL SEARCH REPORT

Inter. Appl. No.

PCT/GB 94/01184

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 5 C08K5/00 C08L67/04 C08L101/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C08K C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 523 789 (SOLVAY) 20 January 1993  see claims 1-9	1,2,4, 13,20, 24,29,30
X	US,A,5 169 889 (KAUFFMAN ET AL.) 8 December 1992  see column 3, line 32 - line 50; claims 1-11	1-9, 11-14, 18-23, 29,30
X	WO,A,92 20738 (BATELLE MEMORIAL INSTITUTE) 26 November 1992 see claims 1-44  --- -/-	1,3,6-8, 29,30

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

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Date of the actual completion of the international search

19 August 1994

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# INTERNATIONAL SEARCH REPORT

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Int. Appl. No.

PCT/GB 94/01184

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